

# PATENT ABSTRACTS OF JAPAN

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## (54) FILM FOR BIODEGRADABLE PROTECTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a film for biodegradable protection that is useful for the protection of large articles that especially have complicated shapes such as automobiles and that has biodegradability and excellence in thermal resistance and shape followingness.

**SOLUTION:** The film for protection consists of an adhesive layer provided on a supporting base material and the rear side of it and the supporting base material consists of a compound made up of a biodegradable plastic (component A) whose glass transition point is below 0 and the biodegradable plastic (component B) whose melting point is above 130. The blend ratio of A and B of the film for protection is 90-60:10-40 by a weight standard. The film for the protection is for the protection of an automobile body.

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- 3.In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the film for protection of the biodegradability for protecting a subject from a crack or dirt. It is especially quality products, such as a car, and is related with the suitable film for protection to protect the object which has large-sized and complicated shape and in which heat resistance is demanded.

[0002]

[Description of the Prior Art]In conveying quality products, such as a car, in order to prevent the value from falling by a crack, dirt, or discoloration during transportation, the film for protection is used. The polyolefin system film has been conventionally used abundantly as a film for this. Since it tends to have followed the form even if it is a to some extent complicated-shaped object, since it is soft and a polyolefin system film has a certain amount of ductility, it was a raw material suitable as a film for protection. However, the quantity of the film for protection used in order to protect the product mass-produced like a car reaches a considerable quantity. After they finish the purpose of use, it is removed and, in almost all cases, is discarded. Under natural environment, in order to hardly decompose, a polyolefin system film will remain in the ground semipermanently, after [ use (for example when reclaimed land and carried out) ]. When abandoned by the ocean, a scene may be spoiled, or the living environment of a marine organism may be damaged, and waste treatment serves as a big social problem. When destroyed by fire, big energy is needed for incineration and there is a problem of generating poisonous gas depending on a presentation and a compound.

[0003]In order to avoid such environmental pollution, the motion which substitutes a biodegradable film for such a film for protection used in large quantities is increasing, and it asks strongly. The resolvability adhesion film which decomposed into JP,6-330001,A by the natural environment which provided the adhesive layer in one side of the base film, and adjusted catabolic rate is indicated. Lactic acid system polymer is used for a base film, and the copolymer of polylactic acid, lactic acid, and hydroxycarboxylic acid is especially used as lactic acid system polymer. However, since its rigidity is comparatively high, lactic acid system polymer is lacking in flattery nature to complicated shape, and since it cannot fit a protector article easily, the fitness as a film for protection is insufficient [ polymer ].

[0004]The sheet for biodegradable automotive coating protection which becomes JP,9-254328,A from the adhesive layer formed in a biodegradable base film and its one side is indicated. In order to prevent

degradation of the automotive coating by the transmitted light and a binder to this protective sheet, paints are blended as an essential ingredient. As a biodegradable base film, polylactic acid, polybutanoic acid, the Pori Glico lids or these derivatives, and others are indicated. However, in addition to biodegradability, \*\* heat resistance and \*\* gestalt flattery nature (moderate elongation and breaking strength, pliability) are required of the protective film used as objects for protection, such as a car. On the other hand, since each protective film currently indicated with the above-mentioned advanced technology has high rigidity and elongation is small, the flattery performance which can follow a complicated gestalt is not fully satisfied.

[0005]

[Problem(s) to be Solved by the Invention]This invention tends to provide the film for protection of a car etc. which has complicated shape especially, and is a film for protection useful for protecting a large-sized article, and has biodegradability, and was excellent in heat resistance and gestalt flattery nature.

[0006]

[Means for Solving the Problem]This invention is a film for protection which consists of an adhesive layer provided in the rear-face side of a supporting substrate and a supporting substrate, Biodegradable-resin; and B ingredient whose A ingredient:glass transition point the above-mentioned supporting substrate is 0 \*\* or less and whose melting point is 125 \*\* or less: The melting point is related with a film for protection of biodegradability which consists of a mixture of not less than 130 \*\* biodegradable resin \*\*. The mixing ratio of A and B is a weight reference, and especially this invention relates to the above-mentioned film for protection which is A:B=90-60:10-40. In a film for protection of above-mentioned this invention, A ingredient which constitutes a supporting substrate, Preferably Polybutylene succinate, polybutylene succinate terephthalate, A polybutylene succinate horse mackerel peat, polyethylene succinate, It is chosen from polybutylene succinate carbonate, a polybutylene terephthalate horse mackerel peat, polybutylene succinate horse mackerel peat terephthalate, polycaprolactone, ornamentation starch, and these denaturation things. Preferably, B ingredient is independent out of copolymers of polyhydroxy butanoic acid, polylactic acid, hydroxybutyric acid, and lactic acid, and these denaturation things, or is chosen as two or more sorts of mixtures. In the above-mentioned film for protection, although common binders, such as a synthetic rubber system and acrylic, can be used for an adhesive layer provided in the rear-face side of a supporting substrate, it is preferably chosen from biodegradable resin and/or a natural product presentation. This invention relates to the above-mentioned film for protection on which the transparency of a film was reduced by carrying out satin finish of the surface side of a supporting substrate as one mode. Especially this invention relates to the above-mentioned film for protection which is an object for protection of a car body.

[0007]

[Embodiment of the Invention]The film for protection of this invention consists of a biodegradable supporting substrate and an adhesive layer provided in the one side (it carries out the rear-face side). A biodegradable supporting substrate is a mixture of A ingredient which is biodegradable resin whose glass transition point is 0 \*\* or less and, whose melting point is 125 \*\* or less, and B ingredient whose melting point is not less than 130 \*\* biodegradable resin. It is a weight reference, and as for the mixing ratio of A ingredient and B ingredient, A:B=90-60:10 - 40 are preferred, and especially 85-65:15-35 are preferred. For the supporting substrate with such composition to be biodegradability In addition, since it has pliability and moderate elongation, Also when it excels in the complicated shape of the object which should be

protected, for example, an automatic car body curved surface, and the flattery nature through which it passes, these objects are covered and it becomes an elevated temperature by direct sunlight since it is hard to generate shearing omission and wrinkles and excels in heat resistance, it has the feature of not producing a big dimensional change.

[0008] Since A ingredient which constitutes the supporting substrate of this invention has the low glass transition point, it excels in pliability and there is sufficient flattery nature to the complicated shape of a protector article in itself, but since the melting point is as low as 125 ° or less, heat resistance is scarce. Therefore, when this is used alone, heat contraction and wrinkles are generated, modification of the coat of a protector article, the storm sewage from the Siwa part, etc. invade, and the summer which becomes a not less than 80 ° elevated temperature by direct sunlight is made to produce corruption of a coat. On the other hand, since B ingredient has a high-melting point, heat resistance is enough, but generally, since a glass transition point is also high, it applies to pliability. Therefore, the flattery nature to the shape of a protector article is missing, and it is easy to generate peeling and wrinkles from an article. It succeeds in this invention by using the suitable mixture of A ingredient and B ingredient as a supporting substrate by having found out that the desirable performance as a protective film was revealed taking advantage of the strong point of both ingredients.

[0009] Heat resistance becomes scarce, although there is little the contribution, it is supple and it excels in flattery nature, when there are few B ingredients than 10 % of the weight. On the other hand, if B ingredient increases more than 40 % of the weight, contribution of A ingredient will decrease, the pliability of a supporting substrate runs short, and flattery nature falls.

[0010] As an A ingredient, specifically Polybutylene succinate, polybutylene succinate terephthalate, A polybutylene succinate horse mackerel peat, polyethylene succinate, Polybutylene succinate carbonate, a polybutylene terephthalate horse mackerel peat, polybutylene succinate horse mackerel peat terephthalate, polycaprolactone, ornamentation starch, and these denaturation things can be illustrated. here -- a denaturation thing -- the above-mentioned copolymerization polymer -- further -- a certain another copolymer component -- copolymerization -- or graft polymerization is carried out.

[0011] It is chosen out of the copolymers and these denaturation things of polyhydroxy butanoic acid, polylactic acid, hydroxybutyric acid, and lactic acid as a B ingredient. These polymers are independent or can be used as two or more sorts of mixtures. here -- a denaturation thing -- the above -- independent or copolymerization polymer -- further -- a certain another copolymer component -- copolymerization -- or graft polymerization is carried out. As such further copolymer component, glycolic acid, a hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid, hydroxyheptanoic acid, etc. are mentioned.

[0012] As for the thickness of a supporting substrate, 5-150 micrometers is preferred. 10-100 micrometers is 20-60 micrometers still more preferably more preferably. In a supporting substrate, various additive agents, such as a filler, paints, an antioxidant, an ultraviolet ray absorbent, light stabilizer, and an antiblocking agent, may be added in the range which does not spoil biodegradability if needed.

[0013] As an adhesive layer provided in the rear-face side of a supporting substrate, binders, such as a synthetic rubber system, a silicone series, acrylic, a urethane system, and a crude rubber system, are mentioned. The rubber composition which consists of high-polymer polyorganosiloxane as silicone pressure sensitive adhesive,  $[(CH_3)_3SiO_{1/2}]_n$  Unit  $[SiO_2]$  What comprises a resin ingredient which is a

copolymer of a unit is mentioned. As acrylic pressure sensitive adhesive, the acrylic copolymer of methacrylic acid alkyl ester and/or the acrylic acid alkyl ester of the carbon numbers 2-14, and ethylenic unsaturated carboxylic acid is mentioned.

[0014]as a crude rubber system binder -- rosin and its derivative (hydrogenation rosin.) The binder which consists of a mixture of one sort or two sorts or more of adhesion grant nature resin chosen from terpenes, such as disproportionation rosin, polymerization rosin, and rosin ester, and the derivative (alpha pinene resin, beta-pinene resin, dipentene resin, and these hydrogenation things) of those and crude rubber is mentioned. The crude rubber used may be a solid or may be latex-like. In these binders, one to adhesion grant nature resin 150 weight section is blended to crude rubber 100 weight section.

[0015]It is preferred to use biodegradable resin and/or a natural product for the adhesive layer provided in the rear-face side of a supporting substrate. Oligomer, a consistency denaturation thing, etc. of resin which have been indicated to be biodegradable resin as an A ingredient are mentioned. Crude rubber, rosin, etc. are mentioned as a natural product. As for the thickness of a binder, 3-100 micrometers is preferred. 3-70 micrometers is 5-50 micrometers still more preferably more preferably.

[0016]To a supporting substrate and/or an adhesive layer, 0.5 or less % of the weight of an antioxidant and/or 0.5 or less % of the weight of an ultraviolet ray absorbent may be added if needed. Each thing generally added by a plastic or the rubber material can use an antioxidant and an ultraviolet ray absorbent.

[0017]The film for protection of this invention can produce a supporting substrate by the general film production methods, such as an inflation and T-die extrusion, An adhesive layer can be formed by applying a binder as a solution of a drainage system or a solvent system, or carrying out heat melting of the b binder, and applying it to the one side (rear face). a) and b -- in [ any ] a method, an adhesive layer may be first produced on a process paper, and it may transfer this to a supporting substrate. Surface treatments, such as priming, corona discharge treatment, and plasma treatment, may be performed to the rear face of a supporting substrate for the adhesive improvement in an adhesive layer. As for a primer, when performing priming, it is preferred to use a biodegradable primer.

[0018]The film for protection may carry out the film production lamination of a supporting substrate and the adhesive layer directly by the co-extruding method. In that case, between a supporting substrate and an adhesive layer, the 3rd layer for the adhesive improvement in both may be provided. As for the 3rd layer, it is preferred to use biodegradable material. As long as it requires, releasing treatment may be performed to the surface side of a supporting substrate.

[0019]As for the film for protection of this invention, except when you need transparency specially, in order to protect a protector article from influence with a beam of light, it is preferred that transparency is low.

Although the kind of A ingredient and B ingredient or its combination can also drop the transparency of a supporting substrate film, the surface side (side which has not provided the adhesive layer) of a supporting substrate is also realizable by giving detailed unevenness to satin finish, i.e., the surface. Satin finish can be performed by various methods and the method in particular is not limited. For example, the method of transferring a crepe roll side by the forming cycle of a film, the method of processing a film surface with a file or sand, etc. can be illustrated. It may be processed by a chemical method in the range which does not spoil not only a physical method but biodegradability. Such crepe processing can also produce the above-mentioned release effect.

[0020]In this invention, with what has biodegradability. After having been discarded by the outdoors, with

the microorganism and dialytic ferment of a nature, it is decomposed into water and carbon dioxide within fixed time, and a \*\*\*\*\* thing is said automatically, Specifically in the examination of JIS K6950, JIS K6951, JISK6953 or a Law concerning the Examination and Regulation of Manufacture etc. of Chemical Substances biodegradable examination (MITI - law) either, the degree of separation of six months after says not less than 60% of thing.

[0021]

[Example] Hereafter, an example explains this invention in details and concretely more.

It is a polybutylene terephthalate horse mackerel peat (the "eco-flex time" film grade by BASF A.G.; the melting point of 115 \*\*) as example 1A component resins. After carrying out the dry blend of 80 % of the weight of A ingredients, and 20 % of the weight of the B ingredients, using polyhydroxy butanoic acid ("BIOGURIN" by Mitsubishi Gas Chemical Co., Inc.; melting point of 180 \*\*, Tg4 \*\*) as Tg-30 \*\* and a B ingredient, the 40-micrometer-thick supporting substrate film was produced with the T-die extrusion machine. After performing corona discharge treatment to one side (rear face) of this film, the binder which uses as the main ingredients the crude rubber which added 0.1 % of the weight of phenolic antioxidants and 0.2 % of the weight of benzotriazol system ultraviolet ray absorbers, and rosin was applied to this field by a thickness of 10 micrometers, and it was considered as the film for protection.

[0022] The metal sphere with a radius of 250 mm which performed acrylic melamine system paint was packed so that it might follow with the film for protection of the above-mentioned production judged to 150 mm squares, and the type of packing was fixed by the adhering function of the adhesive layer. After neglecting the thing of this type of packing at ordinary temperature for 24 hours, it was neglected at 80 \*\* for 24 hours. The appearance visual inspection estimated the type of packing after neglect. The result was indicated to Table 1. The below-mentioned method estimated the biodegradability of this film for protection. The result was indicated to Table 2.

[0023] It is a polybutylene succinate horse mackerel peat ("Bionolle 3003" by Showa High Polymer Co., Ltd.; the melting point of 94 \*\*) as example 2A component resins. After carrying out the dry blend of 70 % of the weight of A ingredients, and 30 % of the weight of the B ingredients, using polylactic acid ("Lacty 9030" by Shimadzu Corp.; melting point of 150 \*\*, Tg60 \*\*) as Tg-45 \*\* and a B ingredient, the 40-micrometer-thick supporting substrate film was produced with the inflation molding method. The adhesive layer was laminated like Example 1 and the film for protection was manufactured. In this way, the characteristic and biodegradability as a protective film of the film for protection which were acquired were evaluated like Example 1, and the result was indicated to Tables 1 and 2.

[0024] The film for protection was produced like Example 1 except having made into the supporting substrate what fabricated comparative example 1 polylactic acid ("Lacty 9030" by Shimadzu Corp.; melting point of 150 \*\*, Tg60 \*\*) with the T-die extrusion machine on the film of 40-micrometer thickness. In this way, the characteristic and biodegradability as a protective film of the film for protection which were acquired were evaluated like Example 1, and the result was indicated to Tables 1 and 2.

[0025] The film for protection was produced like Example 1 except having made into the supporting substrate what fabricated the comparative example 2 polybutylene-succinate horse mackerel peat ("Bionolle 3003" by Showa High Polymer Co., Ltd.; melting point of 94 \*\*, Tg-45 \*\*) with the T-die extrusion machine on the film of 40-micrometer thickness. In this way, the characteristic as a protective film of the obtained film for protection was evaluated like Example 1, and the result was indicated to Table 1.

[0026]

[Table 1]

放置条件	包装外観状態	
	常温×24時間	80℃×24時間
実施例1	○異常なし	○異常なし
実施例2	○異常なし	○異常なし
比較例1	×浮きあり <sup>1)</sup>	—
比較例2	○異常なし	×皺、浮きあり <sup>2)</sup>

1) フィルムの剛性が大きく、伸びが小さいため、初期状態で浮きあり。

2) フィルムが軟化、熱収縮を起こす。

[0027]

[Effect of the Invention]The film for protection of this invention formed using biodegradable resin, Since film properties are [ that the good type of packing is maintained ] also good even when neglected under an elevated temperature so that it may be shown from the result of a package examination of an example, since it excels in the flattery nature and heat resistance which met the shape of the protector article, It is suitable as a protective film of the large-sized article which has complicated shape, such as a car.

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[Translation done.]